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Morphological instability of crystals grown from thin aqueous solution films with a free surface

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ABSTRACT

Morphological instability has been studied experimentally in the growth from dilute $Ba(NO_3)_2$ aqueous solution of crystal films with free surfaces. The observation of transitions from faceted crystal to dendrite, and then to fractal-like patterns is presented. The micro-morphologies of these patterns are investigated. It is suggested that the competition between the step movement and the solute transfer in the growth of thin films determines the stability of the faceted crystal corners. The fractal-like pattern is attributed to random successive nucleation, which is induced by the decrease of the nucleation barrier at high supersaturation and the disturbance caused by the competition between surface-tension-gradient and wetting effects.

§ 1. INTRODUCTION

Pattern formation in non-equilibrium situations is a subject of increasing interest and has been investigated intensively both in theory and in experiment over the past few decades (Vicsek 1989). Among the systems which are investigated experimentally, the crystal growth system is of particular interest. In this system, the driving force for pattern formation is well-defined and many efforts have been made to understand the stability problem during interfacial growth. For rough interfacial growth, such as the situation prevailing in many melt growth systems, Mullins and Sekerka (1964) added a perturbation of the shape on a growing interface and then investigated how this perturbation behaves by solving diffusion equations around the growing surface. On the other hand, for faceted crystal growth with strong anisotropy, Chernov (1974) developed a theory to deal with the stability of polyhedra. The interfacial kinetics was found to play a key role in stabilizing the growing morphology. Besides, it has been generally accepted that the growth morphology depends on the driving force during the growing process. In computer simulation, Saito and Ueta (1989) used a lattice–gas model to study the growth morphology in a diffusion field. Their results indicate that for a small chemical potential difference $\Delta\mu$ between the gas and the crystal, the growth form is polygonal. With an increase of $\Delta\mu$, or if it is sufficiently large, the crystal develops into dendrite. Further increase of $\Delta\mu$ results in a fractal aggregate. Another example was presented by Xiao, Alexander and Rosenberger (1988, 1990). They employed a modified diffusion-limited aggregation model and included anisotropic surface kinetics and surface diffusion, to simulate the evolution of the morphology of crystals growing from an incongruent vapour phase. In their work, the growth morphologies from fully faceted to side-branched dendritic growth are covered through

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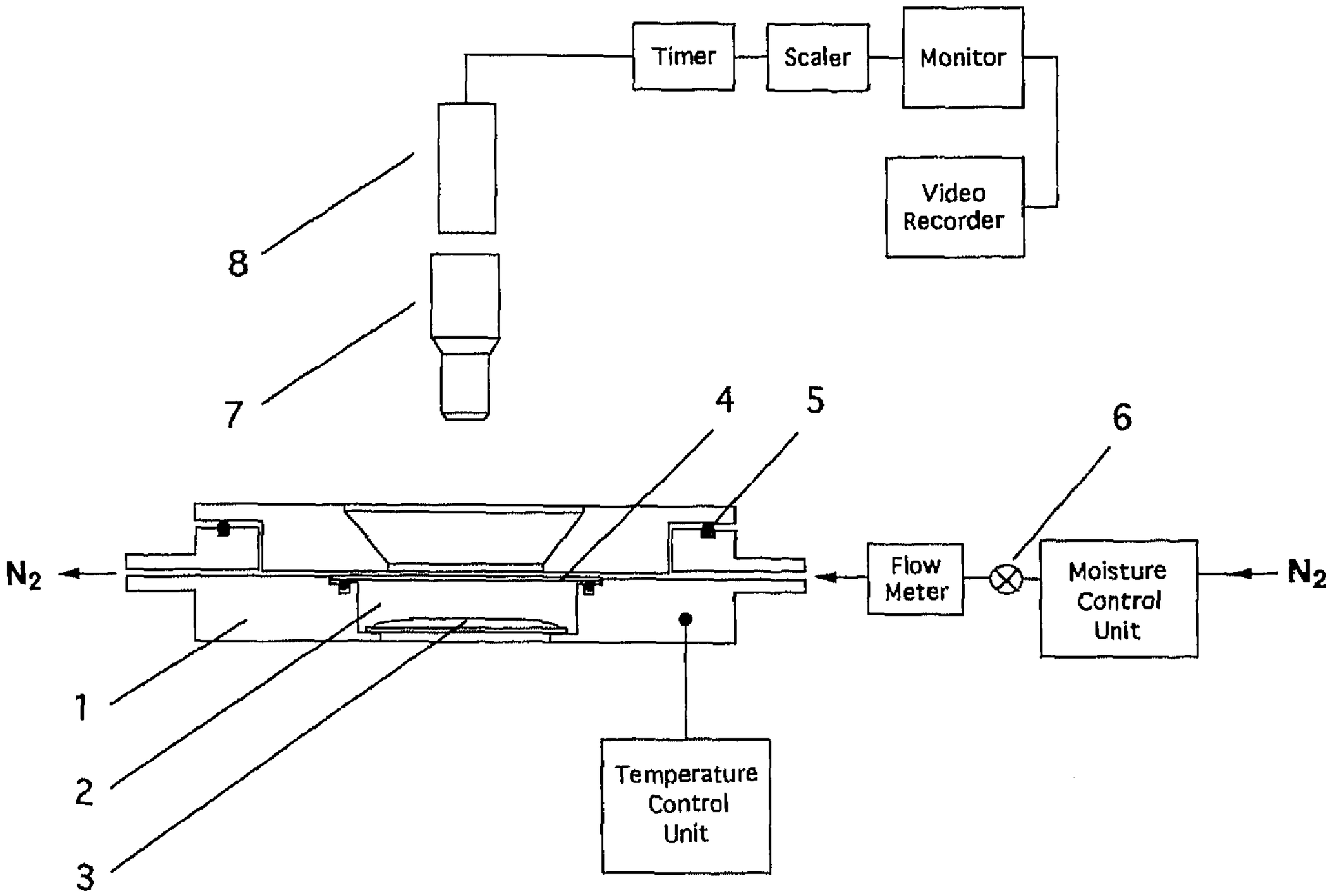
variation of simulation parameters (e.g., temperature, bond strength, supersaturation and surface diffusion). In the case of growth from aqueous solution, as well as the early attempts to study the pattern evolution from polyhedra to dendrites (Chernov 1974, 1984), several recent efforts have been made to investigate experimentally the pattern formation problem (Honjo, Ohta and Matsushita 1986, Raz, Lipson and Ben-Jacob 1991, Ming, Wang and Peng 1993). However, some points remain to be determined. From an experimental point of view, there is still no experimental system which shows all morphologies from faceted crystal to dendrite and to fractals. Besides, although the diffusion-limited aggregation (DLA) model (Witten and Sander 1981) is very successful in explaining some fractal growth phenomena, many important questions regarding the fractal crystal growth mechanisms remain open (Ming *et al.* 1993, Argoul and Arneodo 1990). Because of this situation, in our view more experimental investigations are essential for the further study of the pattern formation problem. In this paper, we report our experimental studies on the morphological stability of polyhedra and the evolution of the morphology from polyhedra to dendritic, and then to fractal-like patterns.

§ 2. Experiments

The experiment was carried out on aqueous solution films of $Ba(NO_3)_2$ with a free surface, mounted on a glass substrate. An evaporation method was used to generate enough supersaturation for crystal growth and to compensate for the decrease of solute concentration during the growth. A schematic diagram showing the experimental set-up is shown in fig. 1. Nitrogen gas with an adjustable degree of humidity is kept isothermal with the chamber and flows through the upper part of the evaporation chamber. In this way, the transport rate of the water vapour between the aqueous solution film and the N_2 flow increases. The pressure of the nitrogen gas is fixed at $1\,kg\,cm^{-2}$. When the partial pressure of the water vapour in the N_2 flow equals the saturated pressure of water vapour in the isothermal system, the whole system will reach equilibrium quickly. In this case, the evaporation rate of the aqueous solution film is zero. When the partial pressure of water in the nitrogen gas is fixed and lower than the saturated pressure of the water vapour in the system, the evaporation rate of the aqueous solution film is kept constant. By controlling the nitrogen flow with a needle valve, the response time of the process described above can be adjusted. In our experiments, the nitrogen flow was $1{\cdot}5\,l/min^{-1}$ and the aqueous solution evaporated at a constant rate. Therefore, supersaturation increased during the growth. However, a typical time for the growth of a fractal or a dendritic pattern is about several tens of seconds, so we suppose that the change of supersaturation during this period should not be very large. Great care was taken to make the glass substrate very clean in our experiments. The cleaned glass plate was wetted by the aqueous solution. Hence a thin uniform aqueous solution film could be formed on it. The initial thickness of the aqueous solution film varied from several tens to one hundred micrometres. $Ba(NO_3)_2$ with a purity of 99·5% was used and the initial concentration of the solution was 9·4%. To eliminate the influence in our system of convection induced by stray temperature gradients, the growth was carried out in an isothermal chamber, with its temperature stabilized at $25{\cdot}00 \pm 0{\cdot}05°C$ by a built-in heating system. Pattern formation was studied under a microscope (Leitz, Orthoplan-pol) and the growing process recorded either on video tapes through a microscope-matched video system or on 35 mm films by a camera.

One of the typical properties of this thin film growth system is that the solute transfer is limited by geometrical restrictions, i.e. due to the fact that the aqueous

Fig. 1



Schematic diagram showing the experimental set-up. 1, copper growth cell; 2, evaporation chamber; 3, glass substrate mounted with an aqueous solution film; 4, lid of the evaporation chamber with many small holes; 5, seal ring; 6, needle valve; 7, objective lens; 8, video camera.

solution film is thin, the gravity-driven convection in the system is suppressed. Therefore, solute transfer is mainly governed by solute diffusion. A typical growth rate for the dendritic and fractal patterns we are studying is about several tens of micrometres per second, while the solute diffusion coefficient in the aqueous solution film is of the order of $10^{-5}\,cm^2\,s^{-1}$. Therefore, the thickness of the concentration boundary layer is about 100 μm. Comparing the thickness of the solution film with the size of the concentration boundary layer, it can be concluded that this growth system is a two-dimensional (2D) one. The second feature is that a free surface of the aqueous solution film exists during the growth, which makes the coupling of the wetting effect and the surface-tension-gradient effect possible. The coupling of these two effects may induce an oscillation of the aqueous solution film (Wang and Ming 1991), which acts as a source of disturbance to stimulate nucleation and generate fractal-like patterns (Ming *et al.* 1993). The third character of our system is that the supersaturation in the system is increasing gradually, which is one important reason why the morphology evolution from faceted crystal to dendritic pattern and subsequently to fractal-like patterns can be observed.

To carry out the crystal growth experiment, the aqueous solution film mounted on the glass substrate was put into the growth cell, and then the nitrogen flow gently adjusted to the value that was calibrated previously. At the beginning of the experiment, the supersaturation is low and the faceted crystal has the morphology of a hexagon. As supersaturation increases, firstly a pyramid, and then, at the bottom of the pyramid, a (100) grown square crystal can be observed. The pyramid-shaped crystal appears as a

result of sudden nucleation on the glass substrate. As the pyramid grows rapidly, the apexes of the pyramid usually become sharp. However, there are two possibilities for the further evolution of the pattern. One is that the apexes are continuously sharpened, which occurs when the solution film is very thin. In this case, dendritic patterns, followed with dense-branching morphology, are eventually generated, as indicated by the filled arrow in fig. 2. A fractal pattern which developed from the apex of a crystal is shown in fig. 3. The fractal dimension of this pattern is $1{\cdot}55 \pm 0{\cdot}03$, which is determined by the sand-box method. However, the densely-branched morphology is not always a fractal. Sometimes it can be a mixture of dendrite and fractals, as indicated by the hollow arrow in fig. 2. When the aqueous solution film is thick enough, the initial distortion on the corner of the crystal may disappear gradually. As illustrated in fig. 4, the sharpened apexes become obtuse and the edges of the crystal become flat. Consequently, the crystal assumes a square shape in a 2D projection (fig. 4 (*h*)). The micro-morphology of the crystals observed in the experiment is illustrated in fig. 5. From fig. 5 (*a*) we can find that additional small crystals have been generated at the corners of the square faceted crystal. These small additional crystals quite possibly evolute from the macro-steps generated from the apexes of the square crystal. Just adjacent to the big square crystal, the additional crystals possess the orientation of the big square crystal. However, as further growth of the corners occurs, the orientation of the small crystals starts to deviate. Figure 5 (*b*) illustrates the micromorphology of the branches of a fractal-like pattern, which is taken far away from the central square crystal. Clearly, the branches consist of many small crystals with random orientations. The crystals along the edges of the branches have clear facets, while those in the middle region have a rough surface.

§ 3. Discussion

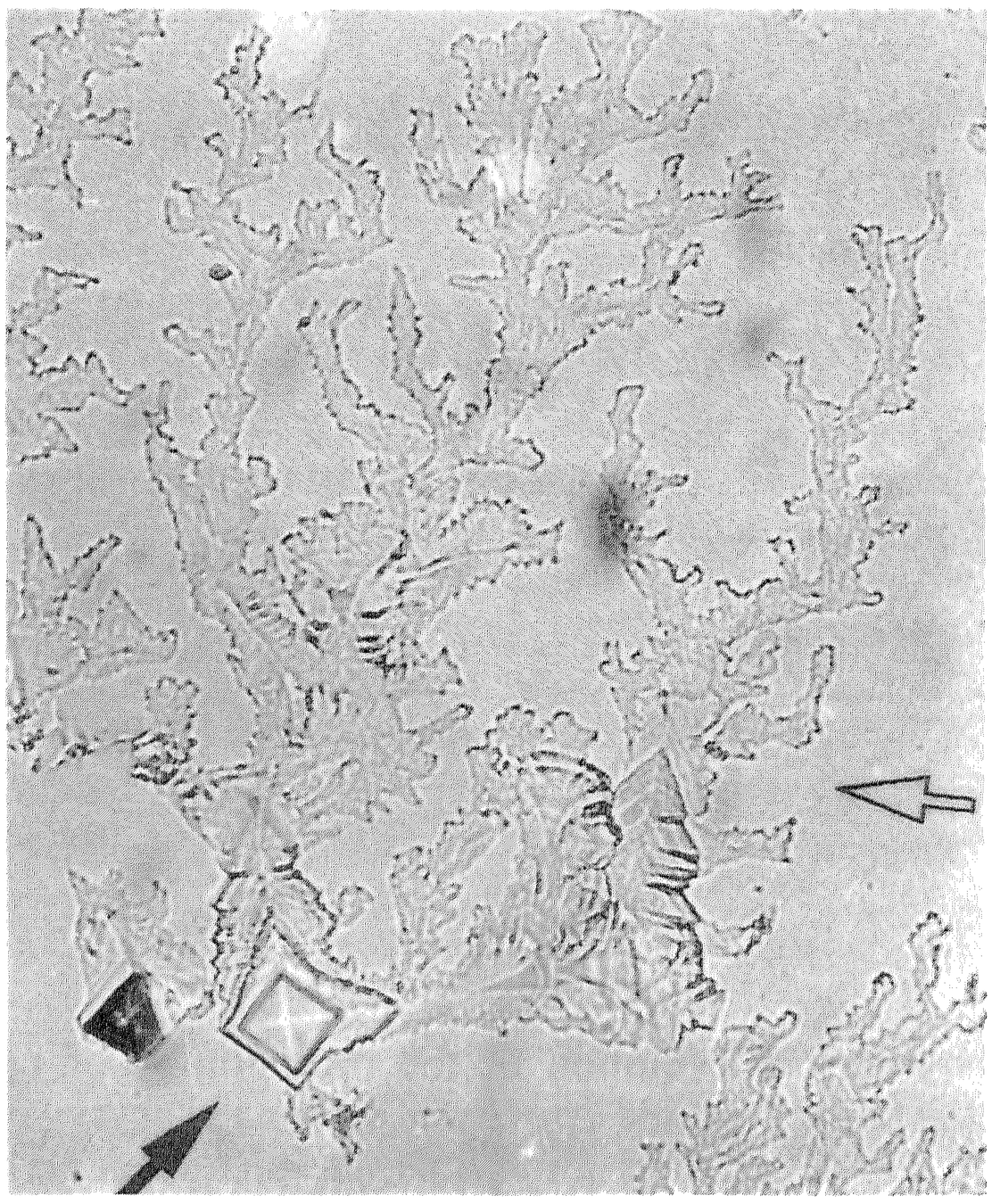
Firstly, we would like to discuss the instability of a faceted crystal and the evolution process from faceted to dendritic patterns. So far, it follows from a number of experimental (Berg 1938, Van Dam and Mischgofsky 1987) and computational (Xiao *et al.* 1990) findings that at the apexes of a crystal, both the concentration and the concentration gradient are significantly higher than those in the central region. In our experiment the evaporation method is employed, which may generate not only very high but also continuously increasing supersaturation. Meanwhile, we suppose that the supersaturation at the corners of the faceted crystal becomes very high and the local nucleation barrier is greatly decreased. Therefore, at the corner of the crystal, nuclei are continuously formed and develop into steps. The continuous step flux generated from the corners moves towards the central part of the facet from the corner region, as schematically illustrated in fig. 6. Let us denote the flux of growth units moving over the crystal surface as j_s, and the flux of nutrient from bulk to surface as j_v. Since the growth of the crystal is assumed to take place only at the steps, for all other places on the crystal surface a simple continuity equation gives

$$\frac{\mathrm{d}j_s}{\mathrm{d}x} - j_v = 0. \tag{1}$$

According to Fick's first law, j_s can be expressed as

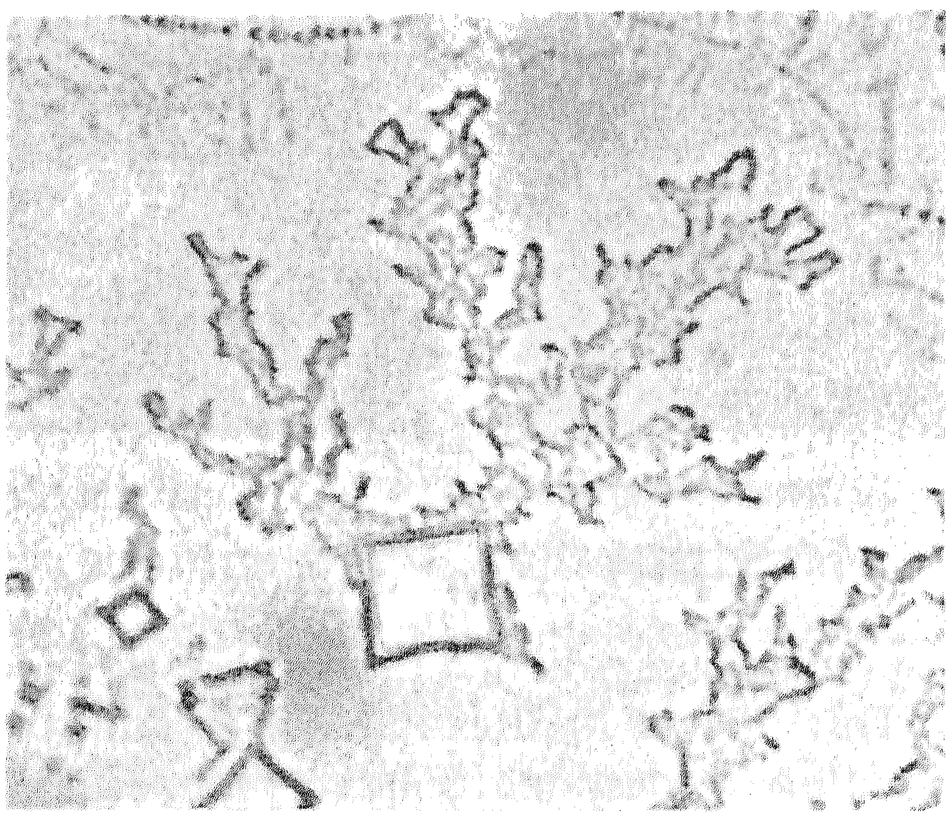
$$j_s = -D_s \frac{\mathrm{d}n_s}{\mathrm{d}x}, \tag{2}$$

Fig. 2



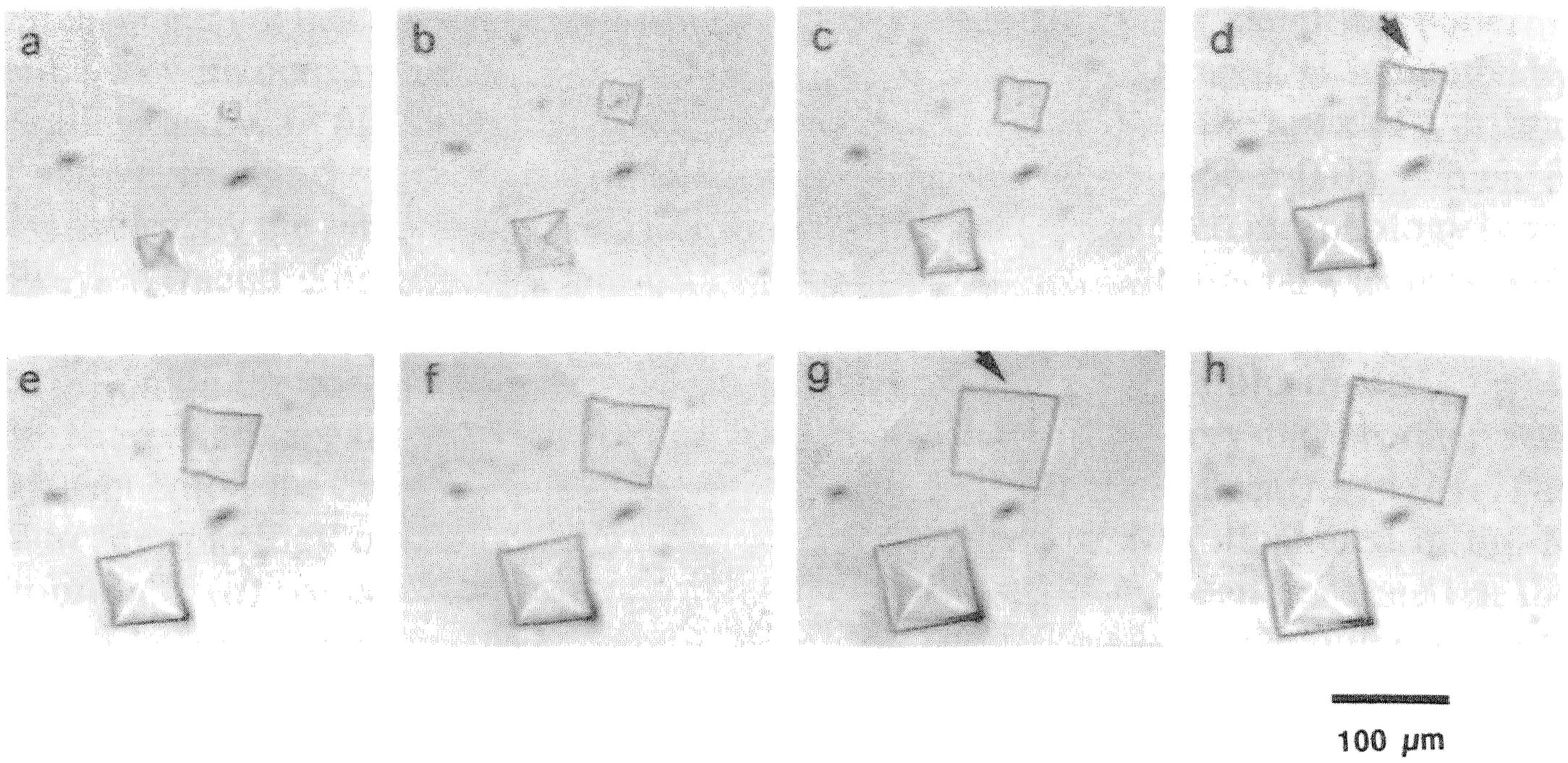
Picture showing the evolution of the growth morphology from a faceted crystal to a dendrite and then a fractal-like pattern. The filled arrow indicates the place where the transition from faceted crystal to dendrite occurs. The hollow arrow indicates the reappearance of a dendrite during the fractal-like pattern growth.

Fig. 3



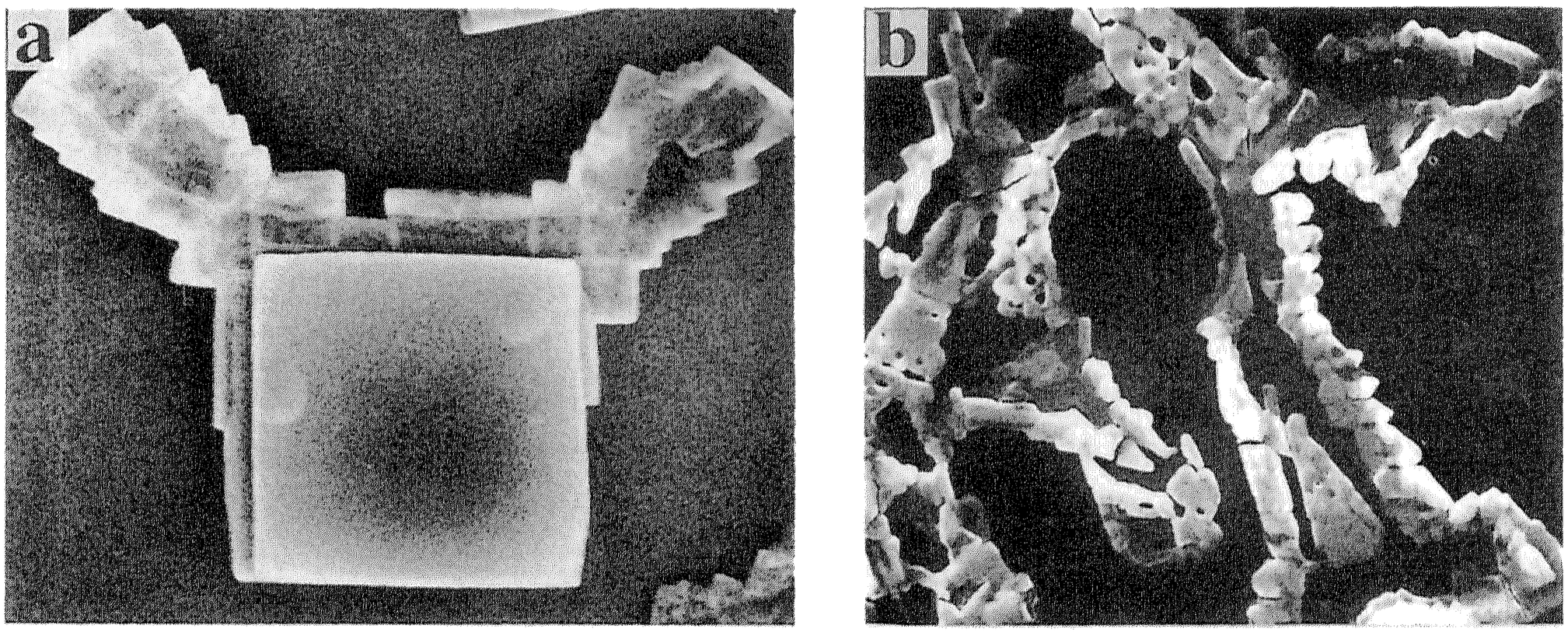
A fractal pattern grown from faceted crystal corners. The dimension of the fractal is 1·55 ± 0·03, which is determined by the sand-box method.

Fig. 4



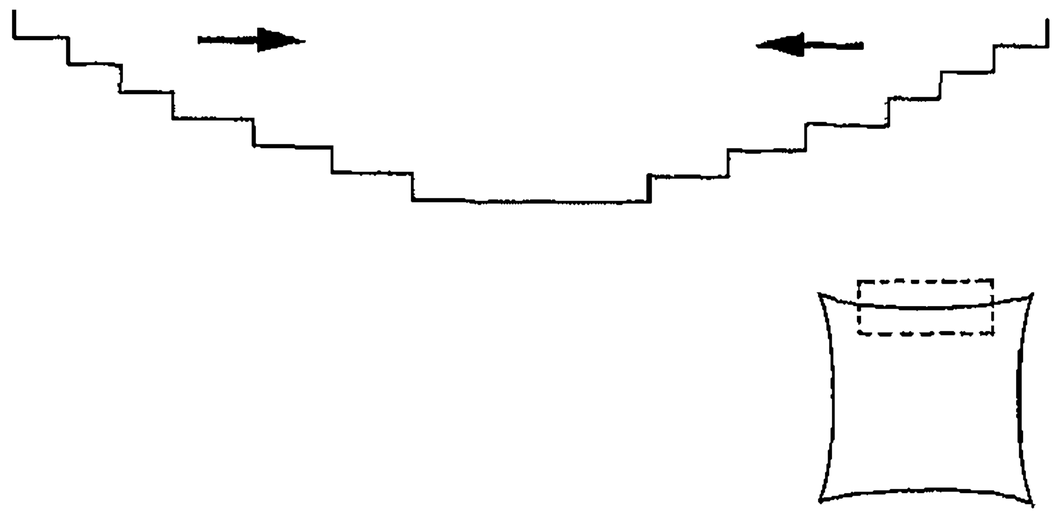
Successive pictures showing the evolution of the morphology of pyramid-shaped crystals. The corners of the square faceted crystal are sharpened at the beginning, as indicated by the arrow in (*d*). However, after some time, the distortion on the edge disappears and the crystal recovers the square shape in 2D projection, as indicated by the arrow in (*g*). This process occurs only when the aqueous solution film is thick.

Fig. 5



(*a*) The micro-morphology at the apex region of a faceted crystal viewed by a scanning electron microscope (SEM). This picture implies that the instability of the macroscopic shape comes from the generation of additional small crystals from the corners or the bunching of microscopic steps during the step movement. (*b*) A SEM picture showing the morphology of a fractal branch. It is clear that the fractal-like pattern consists of many small crystals. The crystals along the edges of the branch possess clear facets, while the crystal surface in the middle region of the branch is roughened.

Fig. 6



The top view of the side plane of a square crystal. The steps are generated from the apexes and move towards the central part of the facet. When two steps moving in opposite directions meet, annihilation occurs and a new facet is formed. The stability of this face is determined by the step advance velocity and the step generation rate at the corners.

where n_s is the surface solute density. Combining eqns. (1) and (2) gives

$$D_s \frac{d^2 n_s}{dx^2} + j_v = 0. \tag{3}$$

Together with the boundary conditions at the steps, which are determined by the relaxation time τ_k needed for a growth unit to enter a kink of a step, an expression for n_s can be found (Burton, Cabrera and Frank 1951). After some simple calculations, it can be shown that

$$j_s = \beta c_0 D_s \frac{n_{s0}}{x_s} \frac{\sinh(x/x_s)}{\cosh(x_0/2x_s)}, \tag{4}$$

where c_0 and β are two factors defined by Burton *et al.* (1951) and Bennema (1967), n_{so} is the number of growth units per unit area in the adsorption layer, x_s is the mean displacement of the growth units on the surface, and x_0 represents the distance between the neighbouring kinks in a step. By using eqns. (1) and (4), the advance velocity v of a straight step can be expressed as

$$v = 2 j_s f_0 = 2 f_0 x_s \tanh\left(\frac{x}{x_s}\right) j_v, \tag{5}$$

where f_0 stands for the surface area occupied by one growth unit in the crystal. It should be pointed out that in real crystal growth processes, the nutrient flux from the bulk to the surface j_v is a combination of both the solute diffusion j_d and convection j_c, i.e. $j_v = j_d + j_c$. If the aqueous solution film is sufficiently thin, the fraction coming from gravity-driven convection in nutrient flux j_c approaches zero. In this case, according to eqn. (5), the advance velocity of the steps will be slower than in the case of a thick aqueous solution film. We argue that the advance velocity of the steps plays a key role in stabilizing a facet when the step generation rate remains constant. As indicated in fig. 6, the steps generated from the two neighbouring corners are moving in opposite directions. When two steps meet, step annihilation occurs and a new facet is formed. For a fixed step height, it follows that the local slope of a face is proportional to the step density according to fig. 6. Under a fixed supersaturation at the crystal corner, the nucleation rate, and hence the step generation rate, is almost constant. Meanwhile,

the step density on the crystal face is governed by the step velocity. In the case of a thick aqueous solution film, the contribution of convection to solute transfer is evident, and the step velocity is high. Therefore, the side face will remain macroscopically flat and the shape will be that of the square crystal. However, if the aqueous solution film becomes sufficiently thin (about 20 μm in our experiment to observe the morphological transition), diffusion will be the main source of solute transfer, and hence the spreading speed of the steps will be slow. However, the steps are continuously generated from the corner of the crystal, and so the step density will become higher near the apex than that in the central part. As a result, the corners of the crystal are sharpened. It should be mentioned that the increase of step density near the corner may lead to a higher solute consumption at the corners. In most cases the increase of step density will decrease the local supersaturation. Hence the corners of the crystal will be stabilized (Chernov and Nishinaga 1987). However, if the supersaturation near the crystal corners is much higher than the critical value for nucleation, we suppose that the decrease of solute concentration caused by the step growth is not sufficient to influence the nucleation process greatly; hence the tips are continuously sharpened. We should point out that with the sharpening of the crystal corner, the tip of the crystal corner becomes further extended into the region of higher concentration. Therefore the local concentration gradient and the supersaturation can be further increased. This means that the nucleation rate at the apexes of the crystal becomes higher, which in turn stimulates the further sharpening of the corners of the faceted crystal. When the supersaturation at the sharpened apex becomes high enough, the nucleation barrier will be greatly decreased and growth becomes very sensitive to disturbances. Meanwhile, small disturbances may lead to an avalanche-like randomly successive nucleation and induce the growth of a fractal pattern from the corner (Ming *et al.* 1993).

It is noteworthy that along the face of a faceted crystal there exists a concentration gradient which is pointed from the corner to the central part of the facet. This concentration gradient influences the spreading of the steps generated from the crystal corners. Let σ stand for local supersaturation, which is defined as $\sigma = (c - c_e)/c_e$ (where c and c_e are local solute concentration and local equilibrium concentration, respectively). According to the theory of Burton *et al.* (1951), the advance velocity of a straight step on the crystal surface is

$$v = 2j_s f_0 = \beta c_0 D_s n_{s0} f_0 \frac{\sigma}{x_s} \tanh \frac{x_0}{2x_s} \propto \sigma, \tag{6}$$

so the velocity of a step depends on the local solute supersaturation. The step velocity is not homogeneous over the facet of the crystal. Using computer simulation, Van Rosmalen (1977) found that a sharp concentration gradient may induce step bunching, i.e. macroscopic steps may be generated because of the variation in concentration. This kind of macro-step may block the successive step movement and stimulate further sharpening of the crystal corners. In our experiment, this situation also occurs. Evidence may be found in fig. 5 (*a*), where macro-steps generated from the crystal corners can be seen.

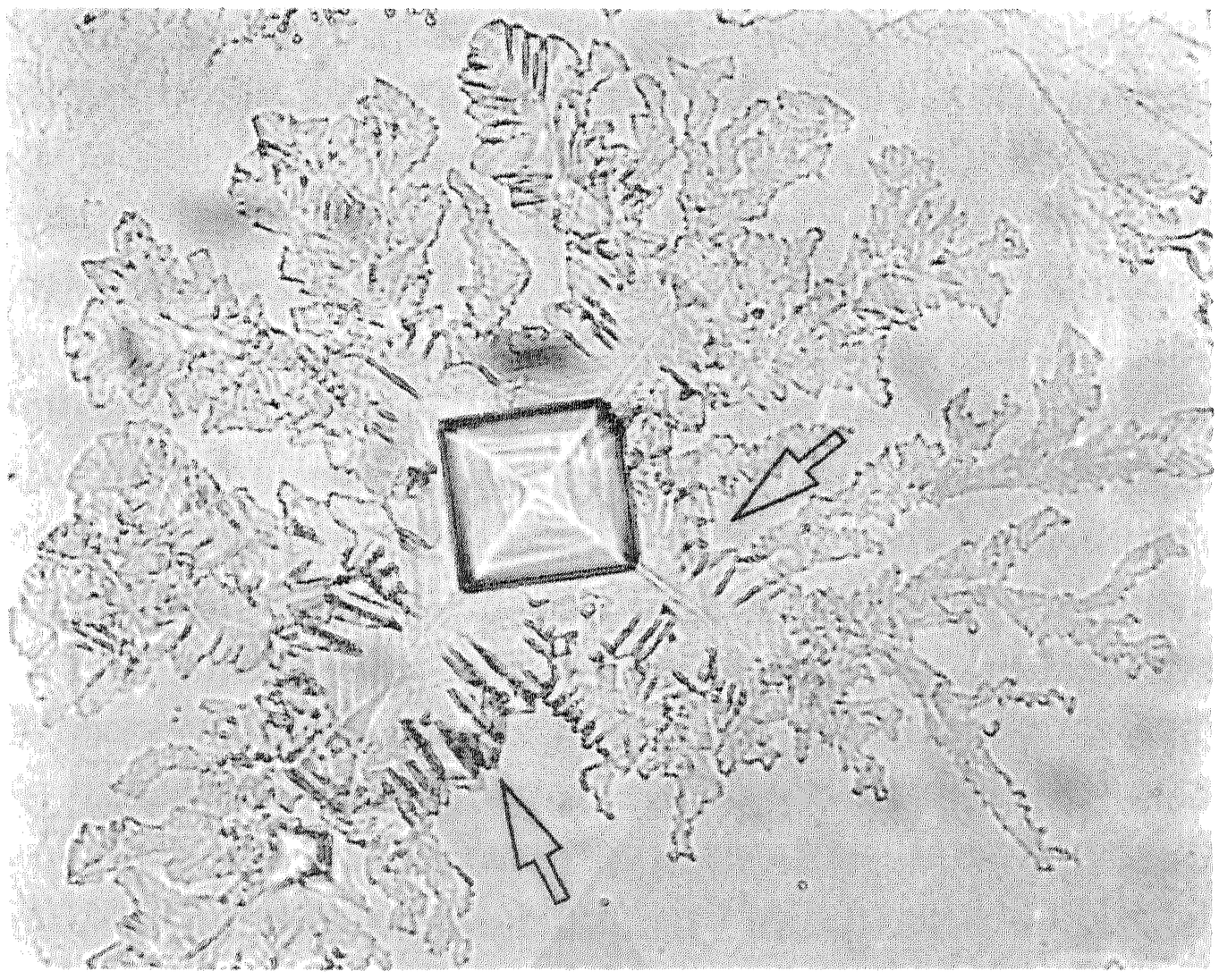
It is a challenge to understand the fractal growth mechanism in our system. In the thin film growth system with a free surface, a gradient in surface tension exists which corresponds to the diffusion boundary layer in front of the growing interface. During the growth, the surface-tension gradient is periodically changing because of the competition of solute depletion within the concentration boundary layer and solute

supply from outside the boundary layer (Wang and Ming 1991). We propose that this periodic change of the surface-tension gradient is responsible for a radial surface-tension wave. The surface-tension wave propagates away from the growing small crystal at the tip of the fractal-like pattern and plays the role of a mechanical disturbance (Ming *et al.* 1993). It is known that in a highly supersaturated system, nucleation is very sensitive to the mechanical disturbance. Therefore, new nuclei will be stimulated around the growing small crystal at the tip of the fractal branch. The generation and growth of these new nuclei will create further disturbances which propagate radically away from the newly generated nuclei and stimulate the formation of the next generation of nuclei. Each time, the newly nucleated small crystals act as the sources of the radially transmitting mechanical disturbance during their growth. The process is self-perpetuating and goes on *ad infinitum*. Consequently, a dense-branching fractal-like pattern is generated. This process is directly controlled by random nucleation. Because the nucleation is a nonlinear process, different from the diffusion process, we call the fractal aggregation process in our case *nucleation-limited aggregation*. A detailed discussion of this nucleation-limited fractal growth model will be presented separately elsewhere.

Figure 2 shows that dendritic and fractal-like patterns are mixed-up. We suppose that this phenomenon is caused by the local fluctuation of supersaturation during the growth of the fractal-like pattern. As we demonstrated previously, the fractal pattern consists of tiny crystals. If the local supersaturation falls for some reason, it is possible that before the resultant nuclei are formed, the already existing small crystals may develop into a dendrite.

Figure 5 (*a*) indicates that adjacent to the square crystal, the small crystals generated along the square crystal edges possess the same crystallographic orientation as the square crystal. Those far away from the square crystal lose this feature. Figure 5 (*a*) only shows the early stage of the development of the pattern. If the crystals grow further, the boundaries between the additional small crystals around the square crystal will finally disappear. Actually, these additional crystals may evolve from the bunched micro-steps, as we mentioned earlier. Therefore it is natural to see that they possess almost the same crystal orientation as the big square crystal. If these 'small crystals' or macro-steps develop further, they may behave like single crystals: fig 7 gives an example. Around the central pyramid, a zone with periodic growth striations can be observed. This zone possesses the same crystallographic orientation as the central pyramid, because we can find the extension of the edges of the pyramid in this area. The region of the dense-branching pattern, however, has neither growth striation nor the extension of the edges of the pyramid. From the shape of the growth striations near the central square crystal, one can find that the corners of the pattern become sharper and sharper as it grows, as shown by the arrows in fig. 7. However, when the pattern develops further, a dense branched pattern emerges instead of the striated dendritic morphology. All these phenomena imply that there are two mechanisms during the evolution of the morphology: the transition of the morphology from square crystal (pyramid) to dendrite should be governed by the competition between the successive generations of steps and the movement of these steps. Meanwhile, the surface kinetics dominates the pattern formation process and the generated pattern is then usually a single crystal. When the supersaturation at the apexes becomes high enough, under the influence of the mechanical disturbance originating from the competition of the surface tension gradient and the wetting effect, nuclei may be randomly stimulated on the glass substrate. In this way, randomly-branched fractal-like morphology is generated.

Fig. 7



Around the central faceted crystal, the growth striations can be observed and the extension of the edges of the pyramid is clear. This means that this region possesses the same crystallographic orientation as the central square crystal. From the shape of the striation, one can find that the corners of the crystal are gradually sharpened, as indicated by the arrows. When the sharpened corners develop further, fractal-like branches are formed. The growth striation cannot be observed on the densely-branched fractal-like patterns.

To summarize, morphological transitions from faceted crystal growth to dendritic crystal growth, and then to fractal-like morphology have been observed. The micro-morphologies of these patterns have been investigated. Based upon the experimental results, we have proposed models to describe qualitatively the observed phenomena. However, quantitative investigations, especially *in situ* monitoring of the thickness of the aqueous solution film and supersaturation during the morphology transitions, are necessary to obtain a more precise picture of the morphological transitions.

Acknowledgments

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References

Argoul, F., and Arneodo. A., 1990, *J. Phys.*, **51,** 2477.
Bennema, P., 1967, *J. Cryst. Growth*, **1,** 278.
Berg, W. F., 1938, *Proc. R. Soc.*, A, **164,** 79.
Burton, W. K., Cabrera, N., and Frank, F. C., 1951, *Phil. Trans. R. Soc.* A, **243,** 299.
Chernov, A. A., 1974, *J. Cryst. Growth*, **24 & 25,** 11–31 and references therein; 1984, *Modern Crystallography III* (Berlin: Springer).
Chernov, A. A., and Nishinaga, T., 1987, *Morphology of Crystals,* edited by I. Sunagawa (Tokyo: Terra), p. 207.
Honjo, H., Ohta, S., and Matsushita, M., 1986, *J. Phys. Soc. Japan*, **55,** 2487.
Ming, N.-B., Wang, M., and Peng, R.-W., 1993, *Phys. Rev.* E, **48,** 621.
Mullins, W. W., and Sekerka, R. F., 1964, *J. Appl. Phys.*, **35,** 444.
Raz, E., Lipson, S. G., and Ben-Jacob, E., 1991, *J. Cryst. Growth*, **108,** 637.

SAITO, Y., and UETA, T., 1989, *Phys. Rev.* A, **40,** 3408.
VAN DAM, J. C., and MICHGOFSKY, F. H., 1987, *J. Cryst. Growth*, **84,** 539.
VAN ROSMALEN, R. J., 1977, *Ph.D. Thesis*, Technische Hogeschool Delft, The Netherlands.
VICSEK, T., 1989, *Fractal Growth Phenomena* (Singapore: World Scientific).
WANG, M., and MING, N-B., 1991, *Phys. Rev.* A, **44,** R7898.
WITTEN, T. A., and SANDER, L. M., 1981, *Phys. Rev. Lett.*, **47,** 1400.
XIAO, R. F., ALEXANDER, J. I. D., and ROSENBERGER F., 1988, *Phys. Rev.* A, **38,** 2447; 1990, *J. Cryst. Growth*, **100,** 313.